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Feasibility of Recovering Useful Salts from Irrigation Wastewater Concentrates Produced by Power Plant Cooling

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Prepared for

Industrial Environmental Research Lab
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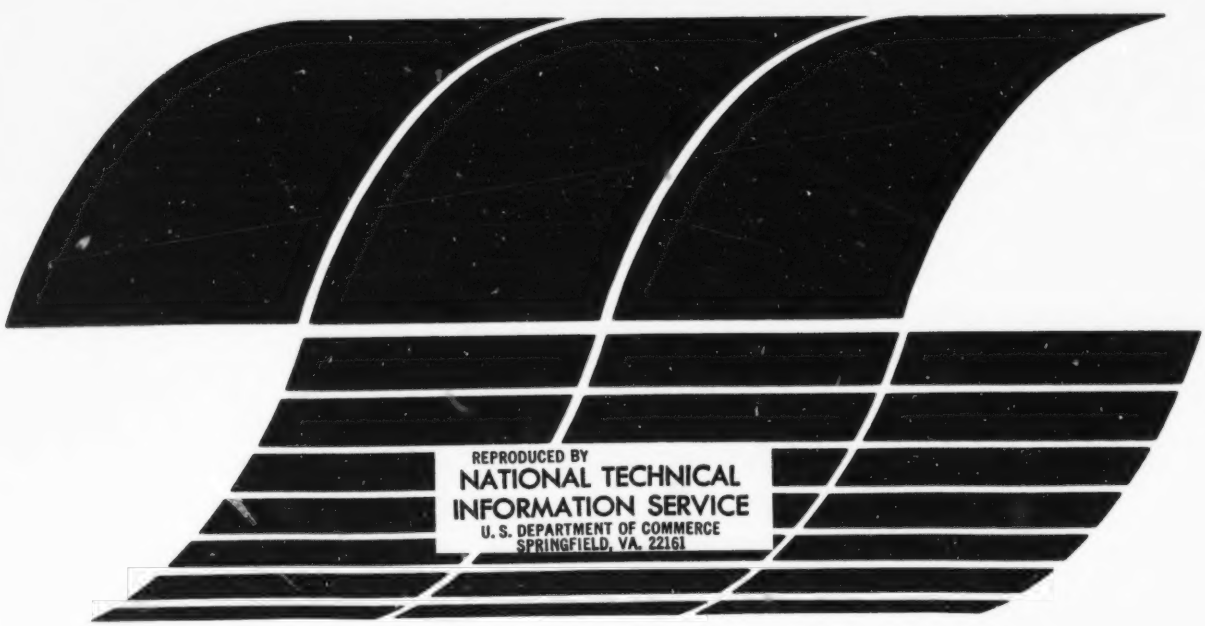
Interagency Energy/Environment R&D Program Report



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Feasibility of Recovering Useful Salts from Irrigation Wastewater Concentrates Produced by Power Plant Cooling

by

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Contents

		Page
Acknowledgements		ii
Figures		iv
Tables		iv
1	Introduction	1
2	Conclusions	3
3	Recommendations	4
4	Introduction: Feasibility of Sodium Sulfate Recovery from Cooling Tower Blowdown	5
	Process and pilot plant design for field test operation	10
	Field test operation at Firebaugh	12
	Comparative cost estimates	15
	Conclusions from the pilot plant tests	16
5	Sodium Sulfate Recovery by Bench-scale Procedures	18
	(a) Recovery of sodium sulfate and its decahydrate from final regenerant effluent	18
	(b) Recovery of $Na_2SO_4 \cdot 10H_2O$ from cooling tower blowdown	19
	(c) Recovery of calcium sulfate	20
6	Sodium Sulfate Recovery by Pilot Plant Procedures	25
	(a) Design, construction and testing of an experimental evaporator-crystallizer with internal product separation	25
	(b) Adaptation of a vertical tube evaporator operated by vapor compression for sodium sulfate recovery, with interface enhancement	28
	(c) Vapor compression, VTFE pilot plant used in this study	29
	(d) Crystallization of sodium sulfate by conventional VC-VTE and by the foamy-flow enhanced VC-VTFE procedure	31
References		36

Figures

No.	Title	Page
1	Flow diagram: proposed power plant coolant cycle	7
2	Pilot plant assembly for field tests on use of agricultural wastewater for power plant cooling	11
3	Field operation of UC-DWR pilot plant, 11/77-2/78	14
4	Sodium sulfate decahydrate crystals on bottom of beaker	21
5	Sodium sulfate decahydrate crystals on paper	22
6	Sodium sulfate decahydrate powder form of crystals after efflorescence	23
7	Evaporator-crystallizer for sodium sulfate recovery	26
8	Vapor compression vertical tube foam evaporator (downflow)	30
9	Evaporation-crystallization of sodium sulfate	35

Tables

1	Agricultural Wastewater Components During Process Cycle	6
2	Solids Recovered from 1000 ML of Regenerant Effluent	19
3	Crystallization of Na_2SO_4 by VC-VTE with Slurry-feed Recycle	33
4	Crystallization of Na_2SO_4 by VC-VTFE Slurry-feed Recycle	34

SECTION 1

INTRODUCTION

The objective of this work was to determine the feasibility of recovering useful sodium sulfate from two types of irrigation drainage water concentrates. These concentrates were obtained during a co-incident field test study conducted by the author and others in the San Joaquin Valley, sponsored by the California State Department of Water Resources (DWR) and power utility entities. That study utilized an experimental cooling tower cycle to assess the feasibility of using irrigation drainage water as coolant; it was coupled with an ion exchange (IX) softening pretreatment of the drainage water feed; the spent ion exchange resin was regenerated with cooling tower blowdown concentrates only. This experimental facility, field test operated in the San Joaquin Valley, provided the concentrated brines used in the study reported here. The results of that associated study has been published elsewhere (1, 2,3). The concentrates from previously softened agricultural wastewater (AW) brines used in this study were the cooling tower blowdown and the final effluent from IX regeneration.

The motivation for this work derived from the promising new procedure permitting the use of irrigation drainage water as a power plant coolant. In that procedure, this wastewater was softened by ion exchange removal of calcium and magnesium rather than by conventional lime and soda addition, to provide brines relatively rich in sodium sulfate. The spent resin was subsequently regenerated solely with the concentrated, softened blowdown brine obtained from the cooling tower during the regeneration step; solid calcium sulfate was precipitated from the concentrated brine. This procedure was demonstrated in a field test series with a pilot plant that provided an opportunity for recovery of sodium sulfate from the two alternative concentrated brines produced in the coolant cycle. Since this wastewater had an initial stoichiometric sulfate content much higher than its chloride content that was also in excess of the combined calcium and magnesium ions, the preferred softening procedure was by cation exchange, reducing both Ca and Mg to about 10 parts per million. The softened wastewater concentrate therefore afforded an opportunity for crystallizing sodium sulfate without concurrently crystallizing magnesium sulfate or sodium chloride. In fact, the removal of some of the sulfate anion appeared advisable to minimize the precipitation of calcium sulfate during the subsequent regeneration of the spent resin with the cooling tower blowdown concentrate. The alternative concentrate from which recovery of sodium sulfate also appeared feasible was the final effluent obtained after regeneration of the spent resin, this effluent would be saturated with calcium sulfate, high in magnesium content and an apparently more difficult source for sodium sulfate recovery.

In addition to the possible commercial value of the sodium sulfate recovered, this EPA-sponsored study also related to the most significant single cost factor in the proposed use of irrigation drainage water as a power plant coolant in the San Joaquin Valley, i.e., the cost of disposal of the final concentrated effluent, for instance, by ponding. By removing part of its sodium sulfate as crystalline salt, the final effluent could be significantly reduced in both its volume and its final solids residue remaining in a solar evaporation pond. As a consequence, this would reduce the size and cost of the solar pond proportionately. In fact the cost of ponding the 20-fold concentrated blowdown was shown to be higher than the combined cost of ion exchange softening the original drainage water feed, the concentration of the cooling tower blowdown by vertical tube evaporation and the regeneration of the ion exchange resin (3).

This study focused primarily upon the feasibility of sodium sulfate recovery by both conventional evaporation-crystallization and by the interface-enhanced, vertical tube foam evaporation technique (4), a novel procedure whereby capital and energy costs may be reduced. This procedure imposes foamy, two-phase (vapor-liquid) flow upon the evaporating liquid to increase its evaporation rate (5,6) or the evaporative heat transfer coefficient. Calcium sulfate precipitated during the ion exchange regeneration procedure was a by-product from the above cooling cycle, and could be of economic value while its recovery would alleviate disposal requirements. The potential for recovering useful sodium sulfate and calcium sulfate from irrigation drainage water had not previously been reported by a similar procedure. If successful, this procedure could reduce by about one third (about $2 million for a 1000 MWe power plant), the cost of ponding the final cooling tower blowdown concentrate after its use for ion exchange regeneration. In addition the potential economic value of the recovered products could provide sufficient incentive for adopting this technology.

SECTION 2

CONCLUSIONS

Bench scale and pilot plant studies conducted on two brine concentrates obtained as the process effluents during field tests on agricultural wastewater for power plant cooling have shown that useful sodium sulfate and calcium sulfate can be recovered from these effluents prior to their disposal by ponding. Recovery of these salts for exportation from a power plant site would reduce the cost of ponding significantly.

Recovery of sodium sulfate, the main objective of this work, was shown to be feasible by evaporation-crystallization utilizing a novel, energy-conserving method. Using this method, foamy vapor-liquid flow imposed upon the evaporating brine-crystal slurry provided enhancement of heat transfer performance up to 40 percent and concurrent energy reductions ranging to 28 percent, compared with conventional, non-foamy evaporation-crystallization of sodium sulfate, in a 5000 gpd vapor compression vertical tube evaporation pilot plant.

The overall conclusions drawn from this and related work are that the use of agricultural wastewater for power plant cooling in the San Joaquin Valley, utilizing ion exchange for pre-softening and its regeneration solely with concentrated brine generated in the cooling process, is feasible and economically attractive. Further, the recovery of sodium sulfate and calcium sulfate from the cooling system effluents prior to their disposal by solar ponding is feasible and provides significant potential advantages. These advantages include a reduction in the size of the solar pond and the market value of the recovered salts.

SECTION 3

RECOMMENDATIONS

Larger scale pilot plant field tests of the recovery of sodium sulfate from the spent ion exchange regenerant obtained as the final effluent in a process system utilizing agricultural wastewater as a power plant coolant should be made. Such tests should provide a sufficient data base for a realistic assessment of both the technical feasibility and the environmental and economic benefits to be anticipated.

The recovery of calcium sulfate, precipitated in an apparently homogeneous form during the ion exchange regeneration and its removal by flotation by the fluidized bed procedure, should be field tested on a larger scale to provide a data base for assessing its commercial potential.

The apparently available markets for sodium sulfate, for instance in paper making and for calcium sulfate, for instance as an agricultural soil conditioner and for wallboard construction should be assessed with reference to the above recommended larger scale tests.

SECTION 4

INTRODUCTION: FEASIBILITY OF SODIUM SULFATE RECOVERY FROM COOLING TOWER BLOWDOWN

The recovery of sodium sulfate from agricultural wastewater after its concentration in a cooling tower was to be examined by two procedures: conventional evaporation-crystallization and vertical tube foam evaporation (VTFE)*. Two different brine concentrates were to be examined: the final effluent after ion exchange regeneration and the cooling tower concentrate before its use in ion exchange regeneration.

The total dissolved solids (TDS) of the agricultural wastewater (AW) collected at the DWR test facility at the Firebaugh site varied seasonally, typically from about 2,000 ppm during the summer to about 6500 ppm in the winter (3). This variation was primarily responsive to rainfall, which peaks in summer, and irrigation practices which depended on the needs of crops being cultivated. During the period of this work, California experienced one of its worst droughts. The result of this was that the TDS of the wastewater remained high (above 3500 ppm), and the silica content was also higher than anticipated; this caused delays in the supply of brine concentrates, occasioned by the need to develop and implement a silica control system for the field tests of the companion study (3).

Table 1 represents the ionic composition of the wastewater and coolant brines during the summer of 1977. Most of the present work was done during the following winter when the wastewater was of approximately twice the concentration (at 7000 ppm of TDS) with about the same solute proportions.

The composition of two brine sources used for recovery of sodium sulfate as the crystalline decahydrate and as anhydrous powder or crystallized Na_2SO_4, is shown in columns 4 and 6 of Table 1, headed "COOLING TOWER BLOWDOWN" and "REGENERANT EFFLUENT", respectively. Of these sources the former suggested assured sodium sulfate recovery, while recovery from the latter was questionable on account of its substantial magnesium and calcium contents as well as a lower sulfate-to-chloride ratio which increases the likelihood of contamination by co-crystallization of magnesium sulfate and sodium chloride. However, the concentrated blowdown would not be available without reservation as a source for sodium sulfate recovery since it also had to serve as the regenerant for the ion exchange (IX) resin after further concentration by vertical tube evaporation (VTE) as shown in column 5 of

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* U.S. Patent Number 3,846,254, November 5, 1974.

TABLE 1. AGRICULTURAL WASTEWATER COMPONENTS DURING PROCESS CYCLE

MAJOR ION CONCENTRATION, mg/l

COMPONENT	AGRICULTURAL WASTEWATER	SOFTENED	COOLING TOWER BLOWDOWN	VTE CONCENTRATE	REGENERANT EFFLUENT
Ca^{++}	346	7	105	150	150*
Mg^{++}	156	6	90	120	3,120
Na^{+}	480	1,190	17,850	23,800	9,600
SO_4^{--}	1,663	1,663	24,945	33,260	19,560*
Cl^{-}	307	307	4,605	6,140	6,140
HCO_3^{-}	528	528	7,920	10,560	10,560
SiO_2	50	50	50*	50	50
TDS	3,530	3,751	55,565	74,080	49,180

*Ca_2SO_4 precipitates during regeneration; *SiO_2 content was controlled.

Table 1. The sodium sulfate content of the blowdown was nearly twice the minimal or stoichiometric requirement as indicated by comparing the Na^{+} and SO_4^{--} ionic levels in columns 5 and 6 before and after IX regeneration. Part of this excess in sodium sulfate could therefore be recovered, provided that it did not reduce the sodium content to a level that would seriously deplete the potential for displacing calcium and magnesium from the spent IX resin during the regeneration procedure (1,2). This procedure would require the recycle of about five volumes of concentrated coolant (column 5) followed by one fresh volume of this coolant concentrate to achieve full IX regeneration. Removal of some of this sodium sulfate would undoubtedly affect the regeneration procedure used in the field test study and would require future adjustments in that procedure.

A flow diagram showing the procedure proposed for the field test study for power plant cooling with irrigation drainage water and also indicating the two proposed withdrawal points of brine for the sodium sulfate recovery of this study is shown in Figure 1.

The second or alternative source for sodium sulfate recovery would be the final IX regenerant effluent having the composition shown in column 6 of Table 1. This effluent would be saturated with calcium sulfate at the temperature used in the regeneration cycle. Its calcium, magnesium, sodium, chloride and bicarbonate contents would also be substantial, providing sources of possible contaminants during the recovery of sodium sulfate by crystallization. This more challenging of the two sources would be more

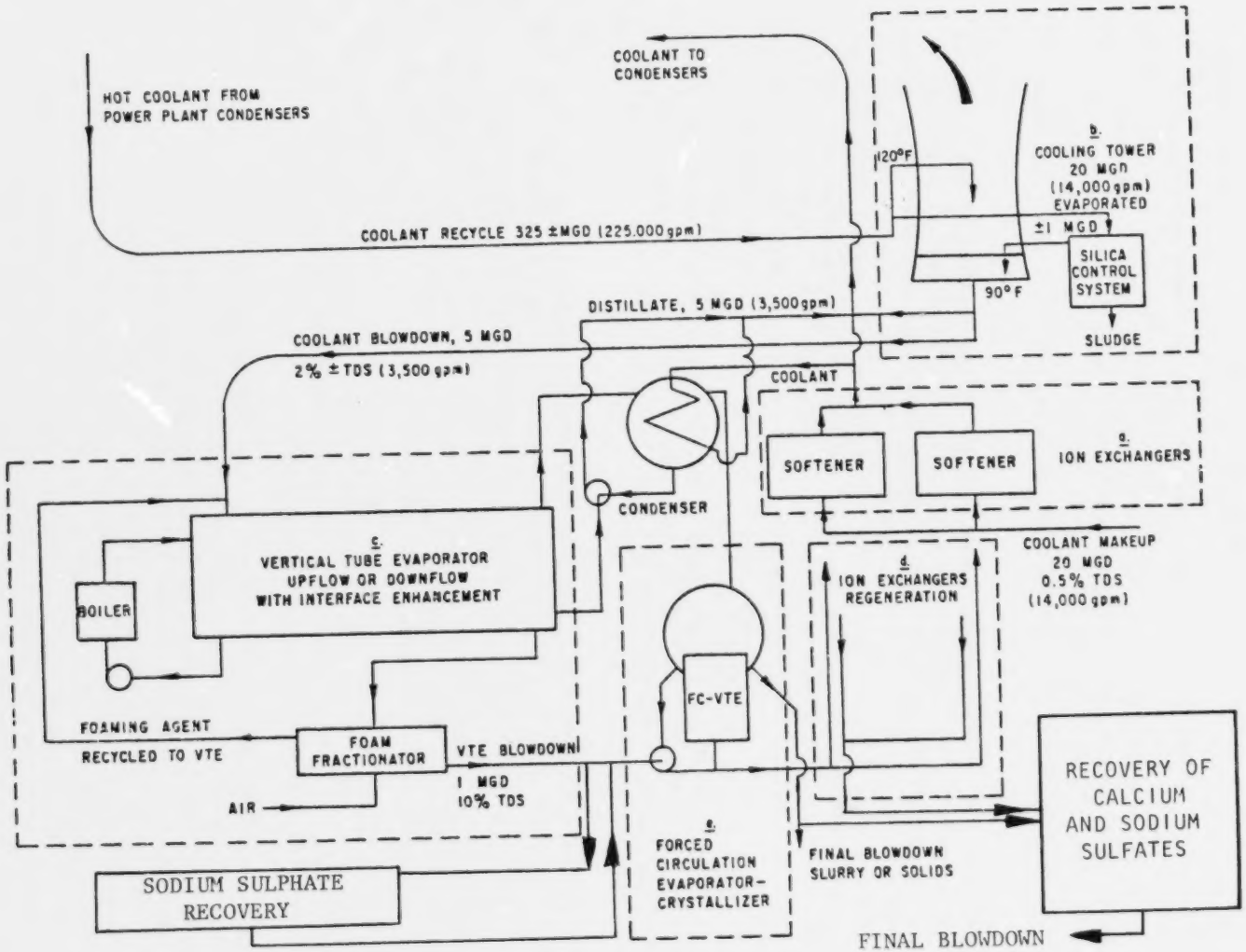


FIGURE 1. FLOW DIAGRAM: PROPOSED POWER PLANT COOLANT CYCLE

acceptable because it would not adversely affect the IX regeneration step of the procedure for power plant cooling by the field tested processes. If it could be proven technically and economically feasible, the removal of useful sodium sulfate from the final regenerant effluent would also reduce the disposal cost of this effluent (i.e., the capital cost of lined solar evaporation ponds for containing the combined salt residues from the final effluent for the life of the power plant). The capital cost of lined ponds needed for a 1000-MWe power plant located in the San Joaquin Valley was indicated to be about $7 million while that of the ion exchange softening, brine concentration and regeneration amounted to about $5 million (3). A capital cost reduction of about $2 million would thus be possible, in addition to the market value of sodium sulfate and calcium sulfate exported from the power plant site.

Fresh water for cooling large power plants in the Southwest has risen in price and declined in availability to the point where irrigation drainage water was selected as the coolant for at least one large proposed power plant, i.e., "Sundesert" planned (but not constructed) for the San Diego Gas and Electric Company near Blythe, California, in spite of the substantial cost of softening pre-treatment that would be required for this hard water and the ponding the saline blowdown brine (7). In addition to the incentive provided by the beneficial use of such wastewaters, further inpetus for development of this potential resource is provided by the concern about its increasing amount, at least in the San Joaquin Valley, where it is anticipated to increase in volume to about 500,000 acre-feed per year containing about 3,000 parts per million (ppm) of total dissolved solids (TDS) by the year 2000. Peak summertime flows of 700 million gallons per day (MGD) was projected within this period (8).

Agricultural wastewater (AW) usually has a high hardness and scaling potential associated with its calcium and magnesium sulfate contents. Its salinity is usually quite high initially (15,000 ppm) but is reduced with the age of the irrigation district due to leaching the soil. Salinity also varies seasonally with the irrigation intensity and rainfall. The TDS of AW in the Southwestern U.S. has a range of about 0,000 to 2,000 ppm. This wastewater effluent often increases the salinity of streams (Colorado River through the Palo Verde drain and the Wellton-Mohawk canal), lakes (Salton Sea) and marshland (San Joaquin and Sacramento Delta) and reduces the fertility of irrigated fields if it is not removed. Using it for power plant cooling could be both economical and environmentally beneficial.

Softening pretreatment is essential to the use of AW for power plant cooling and must be both adequate and economical. Disposal of the concentrated coolant effluent, for instance by discharge into lined ponds to keep these saline concentrates from contaminating surface and ground waters is costly. Two general methods of softening pretreatment are now available: (1) the conventional method of adding lime and soda ash and removal of the precipitated compounds of calcium, magnesium and silica by sedimentation and (2) the novel method of using cation exchange softening and regeneration of this resin solely with concentrated blowdown by a fluidized-bed procedure in conjunction with silica control by treating a small side-stream with alum. This latter method was developed in our Laboratory and was field tested on a

pilot plant scale in the San Joaquin Valley in the joint study with the California Department of Water Resources (DWR), which was co-sponsored by electric power utilities (3).

Conventional methods of softening and silica control will suffice as pretreatment for irrigation drainage water, but they are not cheap, require importation of large quantities of chemicals which add to the salt burden of the final effluent, and are not necessarily the best way to pretreat this wastewater. The use of lime and soda ash addition has been demonstrated to be adequate for Wellton-Mohawk Canal water prior to its desalting by reverse osmosis (RO) and for Palos Verde Drain water used in a pilot plant simulating the proposed Sundesert power plant cooling system (9). The cost of this conventional approach is substantial at about 45 cents per 1000 gallons, and the imported chemicals add to the volume and cost of subsequent ponding of blowdown and softening sludges. In the case of Sundesert, the anticipated daily cost of pretreatment chemicals amounted to close to $5,000 per day, while the anticipated capital cost of the solar evaporation ponds for the effluents was about $17 million for the 2,000 MWe plant proposed (10).

The alternative method of softening by ion exchange (IX) coupled with IX-regeneration solely with concentrated blowdown brine plus silica control by alum dosing of a coolant side-stream provides both capital and operating costs savings. It also permits the recovery of useful salt and reduces the size and cost of ponds for effluents. This pretreatment approach may also be applicable to desalting of AW with RO, and it could be used in seawater desalination in conjunction with the vertical tube foam evaporation (VTFE) technique to permit much higher performance ratios than obtainable before. This approach would conserve energy and reduce the cost of pure water produced.

Several methods of pretreatment and desalination developed at the University of California Seawater Conversion Laboratory (SWCL) provided a new and promising combintion for a power plant coolant process that could use irrigation drainage water. These processes were: (1) the ion exchange softening coupled with fluidized-bed regeneration and (2) the energy-conserving foamy-flow evaporation of brine to be used as regenerant and its clarification by foam flotation. When combined with and serving a cooling tower, this process combination appeared feasible and economically competitive with the conventional approach. The proposal (11) incorporating these combined processes was submitted to the DWR and favorably reviewed by a group of prospective co-sponsors who were subsequently requested to join in the study. Its scope of work was improved by suggestions made during several discussions with representatives of the prospective sponsors, the DWR and the SWCL. The final project plan providing for the design, construction and shakedown testing of a pilot plant facility at the SWCL followed by its field test operation at the DWR site near Firebaugh in the San Joaquin Valley over a total project period of 30 months and at a projected cost of about $600,000 was approved by all co-sponsors for start-up in July of 1975. The project sponsors were the Pacific Gas and Electric Company, the Southern California Edison Company, the Los Angeles Department of Water and Power, and the Electric Power Research Institute in addition to the DWR, and to some extent the University of California and the Water Resources Center.

A favorable environment for this project was also contributed to by the fact that projections of California's future fresh water demands exceeded dependable fresh water supplies (12) and by the California Waste Water Reuse Law of 1974 requiring that wastewater be reused to the maximum extent (13). Also of strong significance was an active interest and co-sponsorship by the Environmental Protection Agency (EPA) in developing these and other related processes. Another factor was the constraints imposed by the EPA guidelines on the discharge of industrial effluents that encourage the increasing use of cooling towers.

The project as planned provided for a meaningful and active co-operation of all interested parties through the submission of quarterly project reports, and their discussion at quarterly committee meetings. The objective was to ensure that the work would be relevant to the needs or interests of the water and power utilities in the State.

The work reported here was a separate but co-incident and related project on the feasibility of recovering useful salt from the effluent of the field test pilot plant operation and sponsored by the EPA, responsive to the above proposal (11) and in continuation of two earlier EPA-sponsored projects (4,14,15,16). The EPA-sponsored work reported here was closely related and integrated with the larger field test project but had separate objectives.

Process and Pilot Plant Design for Field Test Operation

A pilot plant facility incorporating the following process elements and steps was designed, constructed and shakedown tested at the SWCL, transported to the San Joaquin Valley and field tested on AW jointly with the DWR over a 13-month period ending February 1978 (See Figure 2):

(a) Ion exchange (IX) softening of AW collected from an irrigated field to remove calcium and magnesium to residues of about 10 ppm each and replacing these ions with sodium exchanged from the resin.

(b) Evaporation of the IX softened AW by a permissible factor, within the range of 5 to 20, in an experimental cooling tower under process conditions similar to those of a power plant. (Silica scale developed as the main field test problem; an effective and economical method for silica control by aluminum sulfate treatment of a small coolant side stream was also developed and tested during the course of the project).

(c) Further concentration of the 5- to 20-fold concentrated coolant blowdown by the energy-saving vertical tube foam evaporation (VTFE) process (4) to a salt concentration level of 70,000 ppm, sufficient to serve as the sole regenerant for the IX resins used in step (a) above. Clarification of this brine concentrate by a foam flotation procedure (17) to remove both particulates and the foaming agent additive used for the VTFE step noted in (c) was a beneficial and effective procedure.

(d) Regeneration of the IX resin with the brine concentrate using a novel fluidized-bed procedure that simultaneously removes the calcium sulfate

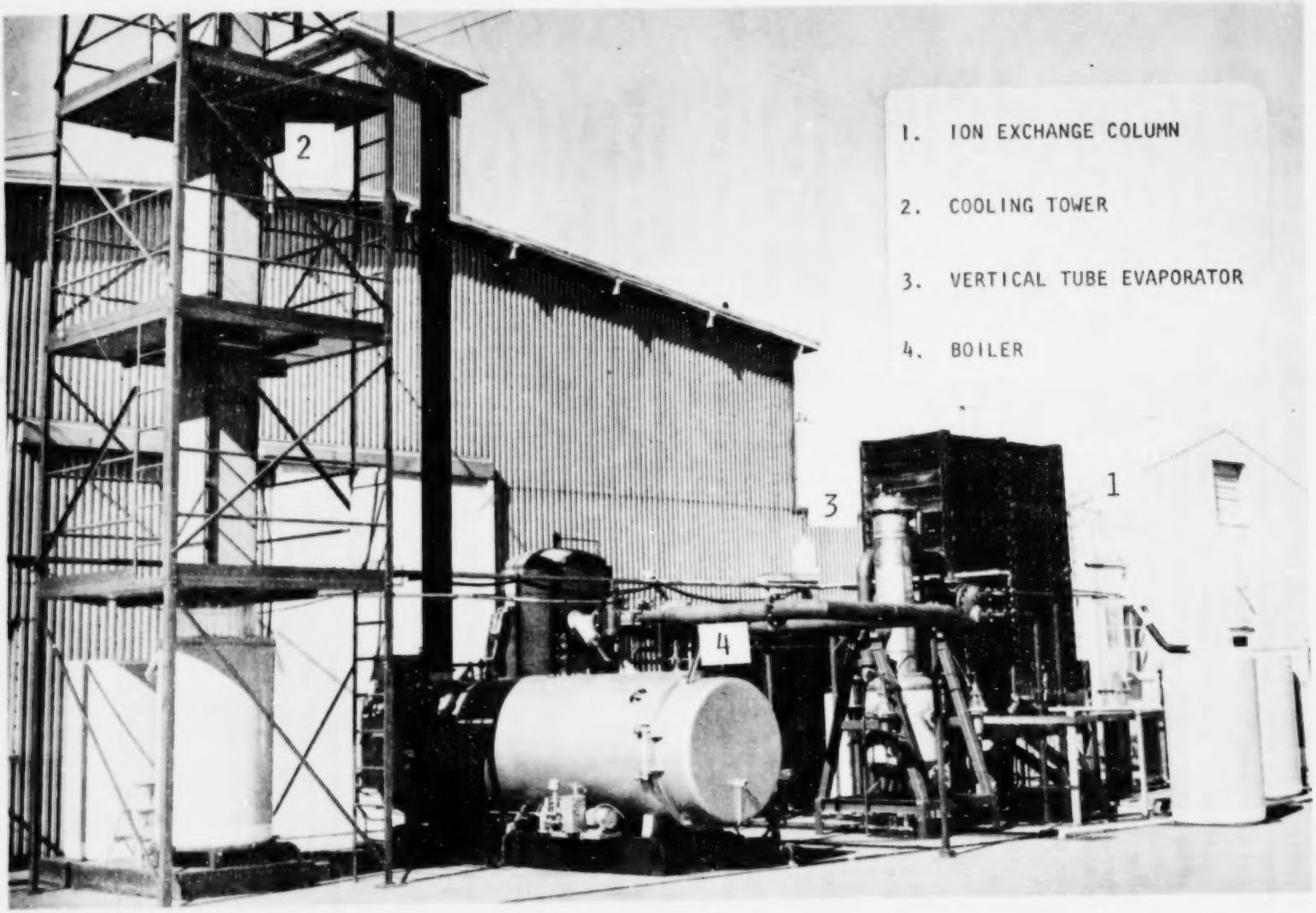


FIGURE 2. PILOT PLANT ASSEMBLY FOR FIELD TESTS ON USE OF AGRICULTURAL WASTEWATER FOR POWER PLANT COOLING.

precipitated during the regeneration process by hydraulic classification (1,2).

(e) Evaporation-crystallization of the concentrated blowdown from this process sequence would provide sodium sulfate as a byproduct and reduce the volume of final effluent to be disposed by ponding.

The integration of process steps (a) to (e) are shown in the flow diagram of Figure 1 with these individual steps enclosed in broken lined blocks. The pilot plant, designed for continuous operation at the field test site, is shown in Figure 2 as assembled at the UC-SWCL during its shakedown testing phase. It included a cylindrical IX softening column of 14-in. diameter, 8-ft high made of Plexiglass and containing a 3-cubic foot layer of polystyrene-divinylbenzene sulfonate resin in the sodium form (regenerated form), and several large vessels for AW feed storage, regenerant storage and recycle. This facility, shown on the right in Figure 2, could produce about 1000 gallons of softened AW per cycle. The custom-made cooling tower, about 30-feet high, is shown on the left of Figure 2. It had a packed section of 20-ft. height and 2-square foot in cross section, similar to a vertical section from the packed core of a large cooling tower. Induced upward air flow and downward flow of coolant through this core were similar to that of a large power plant cooling tower.

Provision was made for controlling the salinity of the coolant within the range of 55,000 and 70,000 ppm of TDS and within a ±1000 ppm fluctuation by utilizing a flow-through salinity sensor controlling the periodic, automatic addition of fresh coolant to the cycle. Blowdown from this cycle was by overflow from the cooling tower basin controlled at either 55,000 or 70,000 ppm of TDS.

The heat input and rejection rate of the cooling tower was 40,000 watts. Heating of the recycled coolant by 20° to 30°F was by passing it at a velocity of about 7 feet per second through 80-foot long copper-nickel condenser tubes heated with recirculated hot water. A 0.8% sidestream of this heated coolant flow of 10 gallons per minute was diverted through the silica control system where it was dosed with 150 ppm of aluminum sulfate, and the precipitated floc containing silica and magnesium was removed by sedimentation and filtration. Immediately to the right of the cooling tower in Figure 2, are the boiler (100 horsepower) and vertical tube evaporator (5,000 gpd) used to further concentrate cooling tower blowdown to the 70,000 ppm of TDS, as needed for regenerating the IX resin bed and to close the cycle. This pilot plant design was detailed elsewhere (3).

The crucial link in this process cycle was the IX resin regeneration with blowdown brine concentrates only. This procedure eliminates the need of softening chemicals and also provides for the possible recovery and sale of potentially useful gypsum and sodium sulfate. Sale of these products would reduce the cost of disposal of effluents, for instance by reducing the size of the pond required.

Field Test Operation at Firebaugh

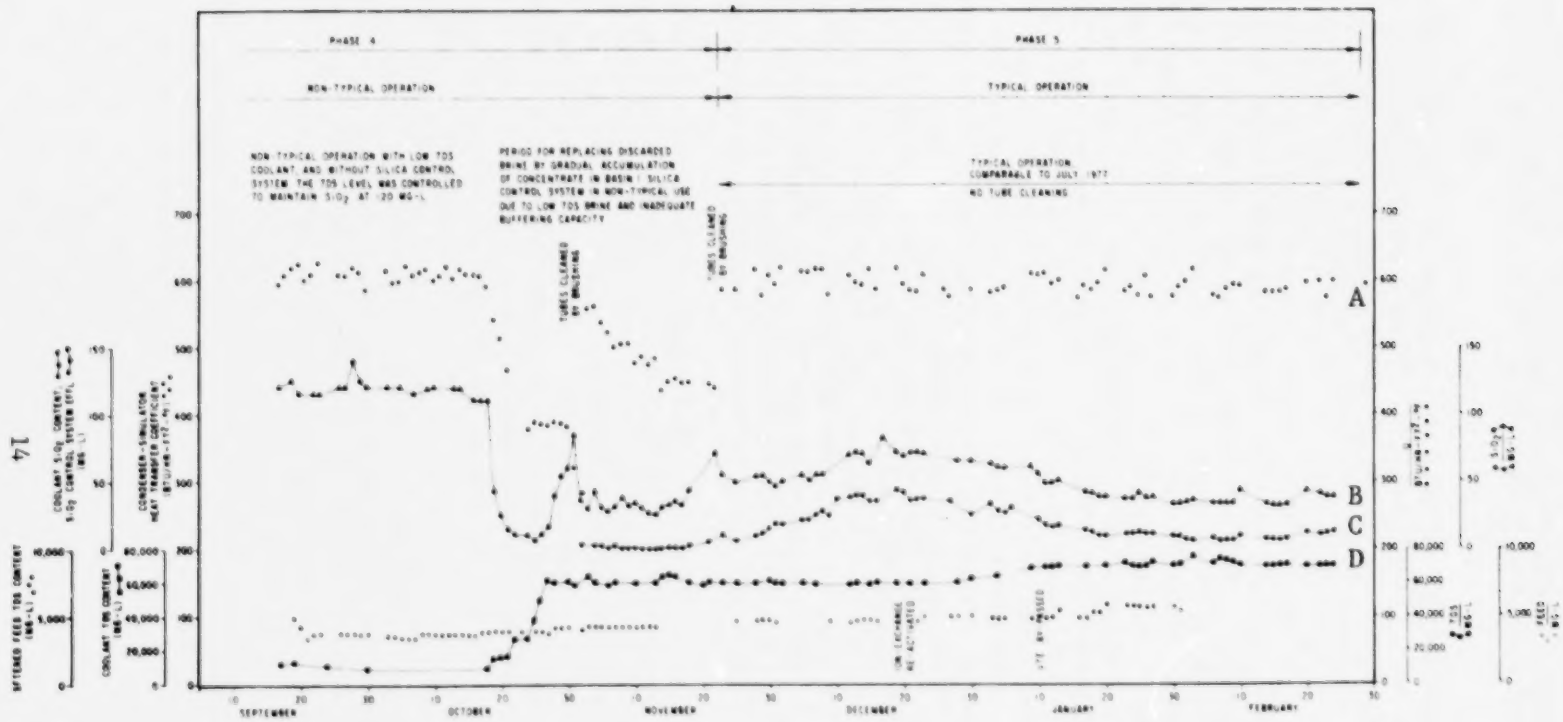
Field operation for a 13-month period of the pilot plant in the San

Joaquin Valley by DWR staff was started in January 1977 with assistance from the staff of the SWCL. These tests were divided into five phases. During The final phase of 3 months duration, all systems were operated in their typical or optimized modes as determined or developed during the preceding four phases. Tests and observations made durig the final (fifth) phase are shown in Figure 3.

The main objectives of this project were achieved during its final phase. These objectives comprised: (1) softening of irrigation drainage water (AW) by conventional ion exchange, (2) using the softened water for cooling in a process that closely simulated power plant cooling, and (3) concentrating this coolant by VTE to a sufficient level for it to be used as the sole regenerant of the ion exchange softening resin. In addition, a process was developed to solve silica scaling, the main unanticipated problem that surfaced during the project. The sidestream silica control system (SCS) proved satisfactory on the basis of each of the following criteria: sustained heat transfer performance, reduction of silica to a level well below its scaling or fouling limits, maintainance of low silica levels at an acceptable reagent cost, and maintainance of alum reagent residual to a level well below its fouling or scaling potential. Plot A in Figure 3 shows that the heat transfer performance of the condenser-simulator did not deviate from its "clean-tube" performance level throughout this period (except for the normal experimental fluctuation of about ±3.5%). In this regard, the best performance data obtained during two earlier periods within the field development phase of the SCS were sustained on an apparently indefinite basis. All other data confirmed this observation; for instance, the silica concentration in the main coolant system remained generally below 50 ppm as shown in plot B, while the scaling/fouling limit had earlier been established as being about three times higher. The SiO_2 level in the SCS outflow was readily maintained below 30 ppm and was as low as 5 ppm (see Plot C). The concentration of aluminum in both the main coolant and the SCS sidestream was in the vicinity of 0.4 ppm, well below the 1 ppm limit generally considered as acceptable.

Confirmation of the effectiveness and adequacy of this SCS was sought by the project coordinating committee through a detailed on-site study by an expert in the field. The consultant supported the above findings for the SCS. He concluded that this method was preferable to the alternative one of using ferric sulfate and his final report of January 27, 1978 also supported the early unit cost estimates for the SCS operation presented to the Committee. This report also supported our findings that floccultion and its settling were favored by the pH of 9 and the TDS of 55,000 ppm of this coolant as field tested. Similarly, he mentioned that the SCS operated well since November 23, 1977, that dissolved aluminum was low, and that our use of an annular filter with adequate intermittent cleaning should suffice to prevent occasional leakage of floc. He also acknowledged that our high TDS brine system was unique in his experience and that our SCS should operate more satisfactorily in a large-scale application than in the pilot plant field tests.

During the final test phase, a series of samples were collected for monitoring dissolved aluminum and silica in appropriate process streams. The data and analytical results obtained by DWR staff at Firebaugh, by the


PHASE 4
PHASE 5
NON-TYPICAL OPERATION
TYPICAL OPERATION
NON-TYPICAL OPERATION WITH LOW TDS COOLANT AND WITHOUT SILICA CONTROL SYSTEM THE TDS LEVEL WAS CONTROLLED TO MAINTAIN SiO_2 AT 20 MG-L
PERIOD FOR REPLACING DISCARDED BRINE BY GRADUAL ACCUMULATION OF CONCENTRATE IN BASIN I. SILICA CONTROL SYSTEM IN NON-TYPICAL USE DUE TO LOW TDS BRINE AND INADEQUATE BUFFERING CAPACITY
TYPICAL OPERATION COMPARABLE TO JULY 1977
NO TUBE CLEANING
TUBES CLEANED BY BRUSHING
TUBES CLEANED BY BRUSHING
ION EXCHANGE RE-ACTIVATED
ACID ADDED
A
B
C
D
SEPTEMBER
OCTOBER
NOVEMBER
DECEMBER
JANUARY
FEBRUARY

PLOT A: CONDENSER HEAT TRANSFER PERFORMANCE
PLOT B: COOLANT SiO_2 CONTENT
PLOT C: SiO_2 CONTENT OF SCS OUTFLOW
PLOT D: COOLANT SALINITY, TDS

FIGURE 3. FIELD OPERATION OF UC-DWR PILOT PLANT
NOVEMBER 1977 - FEBRUARY 1978

DWR-Bryte Laboratory, and by the consultant's laboratory showed sufficient agreement to support the following conclusions:

(1) The silica control system (SCS) was adequate in maintaining the silica concentrations at levels well below the scaling threshold (1 ppm).

(2) Levels of dissolved and total aluminum in the effluent from the silica control system, as well as in the recycled coolant, were maintained at levels well below the suggested maximum level of 1 ppm.

(3) The sidestream SCS was adequate for maintaining high heat transfer performance over about 14 weeks with a recycled softened agricultural wastewater coolant concentration ranging from 58,000 to 70,000 ppm and without any cleaning of the heat exchanger tubes.

Of promising significance was the finding that the cooling tower could be operated satisfactorily on a 15- to 20-fold concentrated softened AW, confirming the early data obtained during the pilot plant development tests at the SWCL (1). As shown in Figure 3 the coolant TDS (Plot D) was maintained at about 58,000 ppm until about December 28, 1977, and then increased to 70,000 ppm and maintained at this level until the end of the project period. Consequently, the VTE could be bypassed, and the cooling tower blowdown was henceforth used directly as ion exchanger regenerant. The capital, operation and maintenance costs of the VTE step could thus be eliminated from the essential process sequence. Alternatively, the VTE facility could be designed for the additional service of recovering useful, saleable salt, such as sodium sulfate from the regenerant blowdown, and used for the latter purpose when not required for cooling tower blowdown concentration.

The alum and brine feed flow rates through the SCS were reduced for the last month of operation, February 1978. The heat transfer performance, and the silica and aluminum levels remained entirely acceptable, indicating that a 0.83 percent sidestream should be adequate. The cost of alum reagent was reduced to a level of about $200 per day for a 1000 MWe plant. This cost might be further reduced when the SCS is optimized with a SiO_2 concentration of about 100 ppm (still below the scaling threshold) in the coolant and in the cooling tower blowdown rather than the 50 ppm limit of these tests.

The VTE was operated satisfactorily, both with the VTFE mode (15 ppm of surfactant added) and the VTE mode (without surfactant addition to the feed), and the heat transfer performance data confirmed earlier data obtained at the SWCL. Overall heat transfer coefficients of about 1800 and 1200 Btu per hr-ft^2-$^\circ$F were obtained with the VTFE and VTE modes (at 160°F), respectively. The surfactant additive was successfully stripped from the concentrated VTFE brine by foam fractionation, and the clarified concentrate (70,000 ppm of TDS) was used for ion exchange regeneration (1,2,3).

Comparative Cost Estimates

Cost estimates were obtained as part of this study by an independent engineering firm during the first phase of the field test series indicated

that this cooling system should be more economical than the conventional lime and soda ash system for this agricultural wastewater as a power plant coolant. This early cost study was reviewed at the conclusion of the field test operation to consider the effects of the two major modifications that were introduced, i.e., addition of the silica control system and deletion of the need for blowdown brine concentration by vertical tube evaporation. This terminal cost review (3) indicated that the revised capital cost of the AW feed and blowdown treatment cost would be as follows for a 1000 MWe power plant using 11.5 million gallon per day of AW coolant feed:

1. Total plant capital cost (excluding disposal treatment of brine by ponding, but including ion exchange pretreatment, silica control, miscellaneous and civil works, contractors overhead and profit at 15%, and a 20% contingincy) amounted to $3,854,000 in 1976 dollars.

The capital cost of providing a pond in the San Joaquin Valley for disposal of the final effluent over the 30-year life of this plant was estimated to be about $7 million (3).

2. Annual cost of AW feed and blowdown treatment (excluding the disposal cost of the final effluent concentrate but including other capital and recurring costs amortized over 30 years at 18% and all operation and maintenance costs and supplies, power, labor, chemicals and SCS sludge disposal) amounted to $1,500,700 based on 1976 dollars; this equates to $0.34 per 1000 gallons of AW treated.

The annual cost of the silica control system (SCS) used was based on the non-optimized field tests and amounted to $169,600 which should be reduced when the SCS is optimized for this application.

The capital cost of ponding the final concentrated effluent would be reduced by about 33% if sodium sulfate is recovered from this effluent and sold. This potential saving of $2.31 million in capital costs plus the capital cost of a conventional softening system (lime and soda ash) would be deductable from the above capital cost of $3.854 million for this cooling system.

Conclusions Drawn From The Pilot Plant Tests

The following conclusions and recommendations derived from the field tests conducted in the San Joaquin Valley:

1. Softening of agricultural wastewater by ion exchange and its regeneration entirely with concentrated softened AW of 70,000 ppm of TDS, is feasible as a pretreatment method for using AW for power plant cooling and economically attractive.

2. The necessary concentration to provide regenerant brine (70,000 ppm) can be done in either a vertical tube evaporator (VTE) or in the cooling tower, thus eliminating the need for blowdown concentration by VTE if this

high a coolant TDS is acceptable from the standpoint of corrosion and cooling tower drift emission.

3. The silica content of the AW supply at Firebaugh was higher than anticipated (up to 50 ppm) during the test period. The silica control system, based on a 0.8% sidestream treated with aluminum sulfate, developed in this project for this purpose was satisfactory and effective; it maintained silica and aluminum levels well below their scaling limits and enabled a continuous 3-month period of operation without any significant degradation in the performance of the heat exchanger, which maintained an overall heat transfer coefficient of 3378 W per m^2-^oC (595, ± 3.5% Btu per hr-ft^2-^oF).

The cost of chemicals for silica control appear reasonable at about $200 per day for a 1000-MWe plant. This cost could be reduced by lower AW silica levels and by permitting a higher SiO_2 content in the recycled coolant and blowdown.

4. The 5000-gpd vertical tube evaporator performed satisfactorily both in terms of heat transfer capability and as a tool for blowdown concentration, and for distilled water production. The cost of this operation would be substantially reduced if waste heat is utilized (i.e., if turbine exhaust steam is used for brine evaporation rather than prime steam) an alternative that is presently being developed under EPA-cosponsorship by the author under a separate project.

5. The foam fractionator performed satisfactorily for stripping surfactant additives and particulate matter from the VTE concentrate prior to its use for ion exchange regeneration.

6. It was shown that the capital cost of solar evaporation ponds required for the disposal of the final effluent from this process sequence was almost twice the capital cost of the ion exchange softening and silica control systems.

7. The capital cost of the effluent disposal ponds could be reduced by about one third if sodium sulfate is recovered from this effluent before ponding it.

8. Further field tests to be conducted on a larger scale, and improvements to permit automated operation of the test facilities, would be advisable before this process is applied for cooling a commercial power plant.

SECTION 5

SODIUM SULFATE RECOVERY BY BENCH-SCALE PROCEDURES

(a) Recovery of Sodium Sulfate and Its Decahydrate From Final Regenerant Effluent.

The clear supernatant brine remaining after regeneration of the cation exchange resin and in equilibrium with precipitated calcium sulfate after stirring this suspension for 1 hour to promote the growth and settling out of larger gypsum crystals at the expense of smaller ones (1,2,3) was used in these experiments. A series of experiments was conducted in which the clear regenerant effluent having 50,000 ppm of TDS (see Table 1) was further concentrated to residual brine concentrations of about 100,000, 150,000 and 200,000 ppm (in 1-liter batches) on a rotary evaporator (Büchi, Rotavapor) under high vacuum, heated with a water bath 45°C (110°F). The first two of these residues remained clear, while considerable cloudiness was noticeable at the highest concentration. This was due to precipitation of a white powdery substance that would not entirely re-dissolve readily upon reheating to 95°C.

These residual brines were subsequently cooled in open glass beakers placed in the refrigerator. Clear chunky needle-shape crystals started growing from the bottoms of the beakers cortaining these concentrates, usually within about two hours and when the brine temperatures were approaching about 4°C (39°F). Crystallization was permitted to go overnight, when the brine temperature was reduced to slightly below 0°C. The brine of the two-fold concentrate remained clear except for crystal and ice formation. The three-fold concentrate deposited a few clouds of fine white, gelatinous-like material in suspension in addition to a preponderance of the large chunky crystalline bars, while the four-fold concentrate had a considerable amount of the suspended white material in addition to the crystalline bars.

The crystals formed overnight upon refrigeration were removed by filtration on a Buchner funnel, followed immediately by washing three times in rapid succession with ice-cold distilled water, and the excess of water removed by suction through the funnel. The residues were partially dried (to a damp condition) by tumbling over filter paper and weighed. The crystalline products were then left exposed to the atmosphere to remove water of crystallization and collapsed into fine white powdery residues which were weighed. Table 2 shows typical results obtained.

TABLE 2. SOLIDS RECOVERED FROM 1000 ML OF REGENERANT EFFLUENT

Concentration Factor (TDS in ppm)	Hydrated Crystals Weight, g.	Anhydride Powder Weight, g.
2 (100,000)	5.7	2.5
3 (150,000)	67.0	27.5
4 (200,000)	69.0	28.0

It was apparent that the weights of the main hydrated crystalline product obtained and its final powdery anhydride were consistent with the expected formation of crystalline sodium sulfate-decahydrate ($Na_2SO_4 \cdot 10H_2O$) which readily loses 10 moles of water on exposure to the atmosphere (efflorescence) and collapses into the powdery, white anhydride (Na_2SO_4).

Further confirmation of the identity of the main crystalline product was obtained by heating these hydrated crystals in an erlenmeyer flask on a steam bath and thus recrystallizing the anhydrous form (Na_2SO_4) from the water of hydration of the decahydrate ($Na_2SO_4 \cdot 10H_2O$) at temperatures above 83°C (181°F). In other experiments, the cooled, three-fold concentrated regenerant effluent when seeded with $Na_2SO_4 \cdot 10H_2O$ would rapidly produce fine needles of the crystalline decahydrate.

Analytical data showed that the composition of the powdery white product was 99.2 percent Na_2SO_4.

Based on these experiments, approximately 40 percent of the total salt content present in the original irrigation wastewater could be recovered as either $Na_2SO_4 \cdot 10H_2O$ or as its anhydride from the final IX regenerant effluent obtained from this experimental power plant coolant system. This recovery assumes an approximately three-fold concentration of this effluent, its temperature reduction to about 0°C to form the crystalline decahydrate (mirabilite or Glauber's salt), or production of the anhydride (thenardite) by further evaporation-crystallization above 83°C (181°F).

(b) Recovery of $Na_2SO_4 \cdot 10H_2O$ From Cooling Tower Blowdown

The cooling tower operated at the Firebaugh site was initally operated with a softened coolant having a TDS level of 55,000 ppm from January through August 1977 and thereafter at a TDS of about 70,000 ppm (November 1977 through February 1978). During the earlier period, the TDS of the cooling tower blowdown was increased to the 70,000 ppm needed for ion exchange regeneration by concentration with vertical tube evaporation (VTE).

Sodium sulfate was readily recoverable from this softened concentrate. This is not surprising, considering that its composition (about as shown in Table 1, column 5) was relatively low in calcium, magnesium, and chloride with reference to sodium and sulfate. It was decided that recovery of no

more than about 50 percent of this sodium sulfate content would be permissible if sufficient sodium ions are to remain in the mother liquors for the IX regeneration step that would still have to be accomplished subsequently.

A series of experiments was conducted to determine the appropriate conditions for sodium sulfate recovery. These tests showed that approximately 50 percent of the available sodium sulfate would crystallize as the deca-hydrate at about 0°C from the softened cooling tower blowdown, if the latter had been further evaporated to a TDS of about 140,000 ppm. This is illustrated by the following typical procedure carried out with blowdown sampled on December 13, 1977, from the San Joaquin cooling tower "Basin I" during its long-term field test operation under optimal steady-state conditions.

Cooling tower blowdown brine having a TDS of 70,000 ppm and an ionic composition sililar to that in column 5 of Table 1 was concentrated to 140,000 ppm by evaporating a 1000-ml volume to 500 ml in a rotating-flask evaporator (Büchi, Rotavapor) under vacuum (oil pump), and using a water bath temperature of 45°C. The clear concentrate was poured into a 1-liter Pyrex beaker and placed in the refrigerator overnight for slow cooling to about -2°C (28°F). Chunky, needle-like crystals measuring about $\frac{1}{4}$-inch x 2 inches developed apparently from the bottom of the beaker in a criss-cross arrangement as shown in Figure 4.

The cold mother liquor was decanted, and the crystals were washed three times in rapid succession by pouring ice cold distilled water over them and decanting. The washed crystals were drained of water, removed from the beaker and dried on a sheet of filter paper by tumbling. The product, allowed to dry in the air and then weighed on a sheet of paper, is shown in Figure 5 (83.0 g). This material was allowed to slowly effloresce (to the open air) to a white powder still having the form of the above crystals (see Figure 6). After complete drying, a white powder weighing 36.3 g was analysed as 100.15 percent Na_2SO_4. These data were consistent with the crystallization of mirabilite ($Na_2SO_4 \cdot 10H_2O$) that effloresced to the anhydride, thenardite with a yield of 51.85 percent based on the total salt content in the softened blowdown from the cooling tower.

It was concluded from these bench-scale experiments that useful sodium sulfate should be recoverable from either the final wastewater effluent, after IX regeneration in a yield representing about 40 percent of the total salt content of the cooling tower blowdown, or directly from this blowdown before using it for IX regeneration, in a maximal 50 percent yield.

(c) Recovery of Calcium Sulfate

The recovery of calcium sulfate was evaluated during this EPA-sponsored part of the overall program for using softened irrigation drainage water as a power plant coolant. Its formation during the regeneration of the IX resin and its separation by hydraulic classification by a fluidized bed regeneration procedure was part of the DWR field test series conducted with the pilot plant in the San Joaquin Valley (1,2,3). A comparison of the ionic contents of columns 5 and 6 of Table 1 indicates that approximately 14,200 mg/l of sodium

FIGURE 4. SODIUM SULFATE DECAHYDRATE CRYSTALS ON BOTTOM OF BEAKER

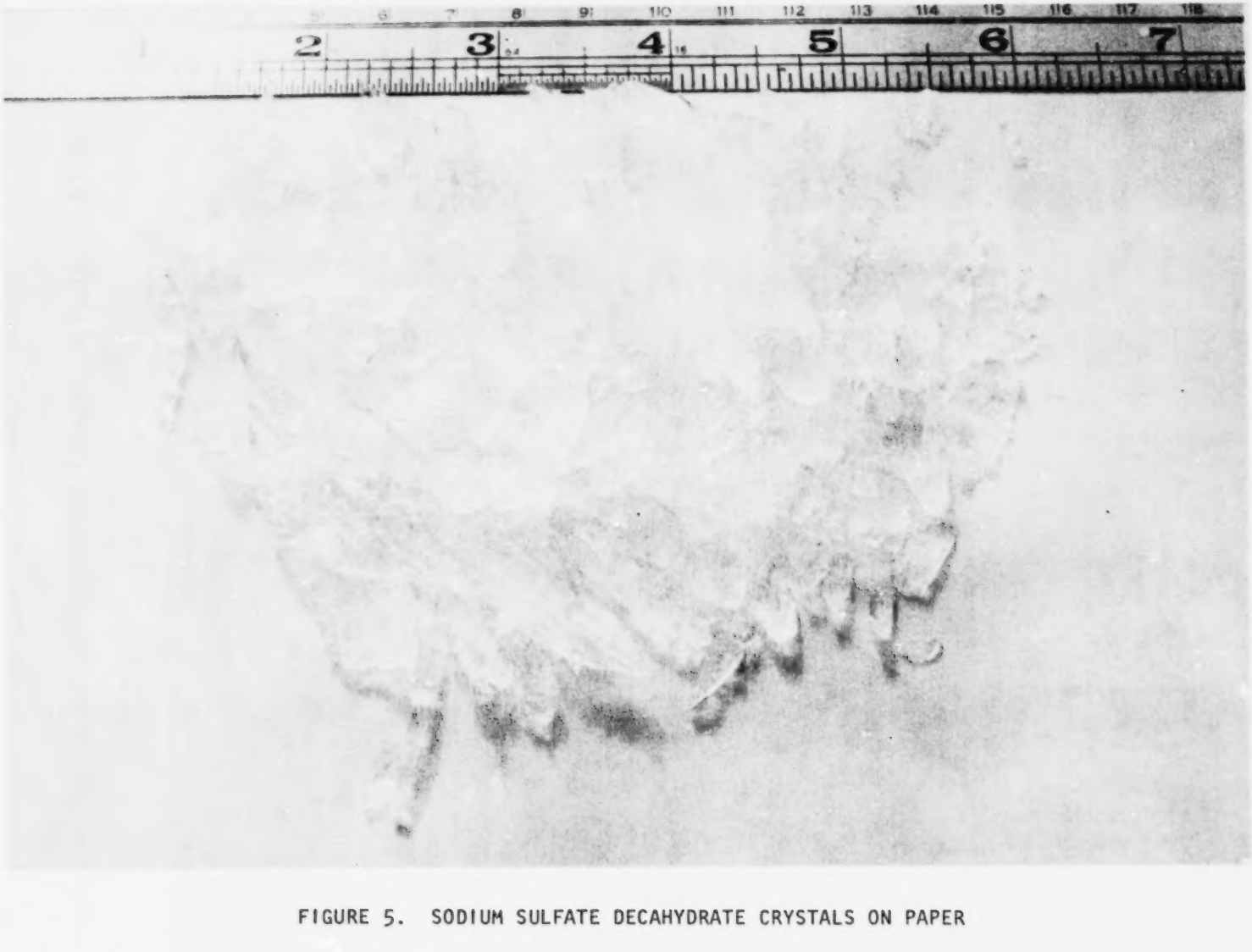


FIGURE 5. SODIUM SULFATE DECAHYDRATE CRYSTALS ON PAPER

FIGURE 6. SODIUM SULFATE ANHYDRIDE POWDER FORM OF CRYSTALS AFTER EFFLORESCENCE

was exchanged for 3,000 mg/l of magnesium, and the remainder was exchanged for calcium of which virtually all would have precipitated as gypsum. This represents about 31,860 mg/l of gypsum precipitated from process brine during the IX regeneration procedure. Gypsum was produced in an apparently homogeneous form. The quantity of gypsum to be anticipated from a 1000-MWe power plant using 11.5 million gpd of wastewater coolant with the cooling system developed in this work, would be approximately 77 tons per day when the coolant has the composition shown in Table. 1. The potential for using this material was not evaluated in this work, but gypsum might conceivably be useful as a soil conditioner or for wall board manufacture. Gypsum produced during IX regeneration was suspended in hot tap water and removed by filtration on a Buchner funnel. This residue was washed well with hot water followed by distilled water washing and dried on filter paper. It analyzed to 98.98 percent $CaSO_4 \cdot 2H_2O$.

SECTION 6

SODIUM SULFATE RECOVERY BY PILOT PLANT PROCEDURES

Two evaporator-crystallizers were constructed and tested in this work: (1) a small and versatile pilot plant utilizing forced re-circulation of brine through a heater followed by flashdown and separation of the crystalline sodium sulfate produced into a quiet zone and (2) adaptation of a 20-cubic meter per day vapor compression vertical tube evaporator for a slurry-feed recycle of brine and crystalline product and crystallization of anhydrous sodium sulfate into the slurry and its subsequent separation by centrifugation.

(a) Design, Contruction and Testing of an Experimental Evaporator-Crystallizer with Internal Product Separation

The pilot plant facility, shown in Figure 7, was modeled after the Oslo type of evaporator-crystallizer. It could be operated at low or high temperatures to crystallize sodium sulfate as its decahydrate, to simulate the use of waste heat for this purpose (by evaporation at temperatures below 50°C (122°F). It also allowed recrystallization of the decahydrate by cooling alone. It was further used to crystallize the anhydride at evaporation temperatures above 83°C (181.4°F).

This pilot evaporator-crystallizer was made of pyrex glass, brass pipe sections and appropriate fittings. It utilized electrical immersion heating with two stainless-steel-sheathed heaters of 3000 W each mounted in a 60-cm (24-in.) long, 7.5 cm (3-in.) diameter Pyrex pipe through which the brine was pumped upward for recycling with a centrifugal pump (stainless steel) while being maintained under sufficient pressure to prevent boiling. The heated brine was then released through a control valve for flashdown into a horizontal Pyrex tube of 120-cm length and a 2.5-cm diameter which was tangentially attached near the top of a separator vessel made of brass and Pyrex pipe sections, 15-cm diameter and 120-cm long, mounted vertically. The top of this separation vessel was attached to a condenser via a short pipe elbow of 5-cm diameter. The body of this vessel was divided into an upper cyclone separation section for disengaging the liquid phase from the flashed vapor and a lower quiet zone for settling out the crystalline product formed by evaporation of the recycled and re-heated brine. This was accomplished by providing a funnel-shaped down-spout to deliver the brine to a central point about 30 cm down into the quiet zone which was about 75 cm in vertical dimension and separated from the cyclone zone by a brass plase. Recycled brine was withdrawn from a level just below this plate. Provision was made for withdrawing the solid phase product (crystals) through a large valve attached

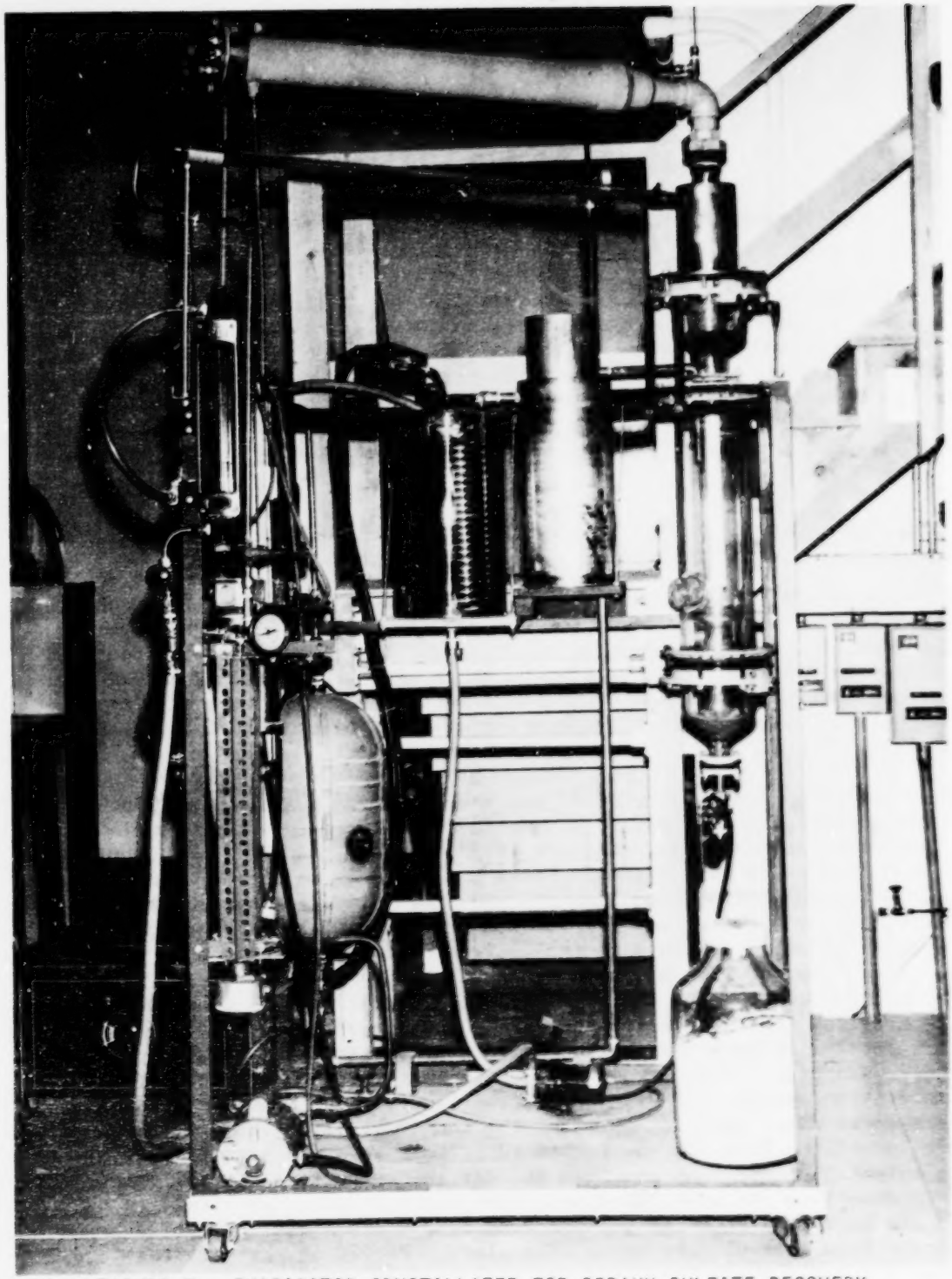


FIGURE 7. EVAPORATOR-CRYSTALLIZER FOR SODIUM SULFATE RECOVERY

to the conical (domed) bottom section of the lower Pyrex vessel.

This pilot plant was operated under vacuum (oil pump, 29.5-in. Hg), and fresh feed liquid was continuously introduced through a valve connected to the preheated brine line immediately upstream of the horizontal flashdown pipe. The condenser was cooled with either tap water passed through a copper pipe coil contained in the horizontal tube condenser or by recycling chilled water through the coil from a refrigerated container. A commercial refrigeration unit having a freon-evaporation coil made of stainless steel connected to an automatic freon compressor and heat rejection unit, shown in Figure 7 (Van Waters & Rogers) was used.

This evaporator-crystallizer unit was used for the recovery and recrystallization of $Na_2SO_4 \cdot 10H_2O$ as well as Na_2SO_4. In one typical application, the evaporator was evacuated of air and cooling tower blowdown transported from the San Joaquin Valley field test site in large polyethylene bottles (see column 5 of Table 1) was introduced under vacuum to fill this apparatus to the level of the cyclone separator. The brine was then recirculated over the electrical immersion heaters, and cold tap water was passed through the condenser. Flashdown of the recycled preheated feed brine usually reached a steady-state evaporation rate at a temperature level of about 40°C (104°F). Evaporation was maintained at this level with the volume being maintained by controlling the inflow rate of fresh brine feed under vacuum and by collecting distillate at an approximately equal flow rate in an evacuated reservoir connected to the condenser.

After about a three-fold concentration level of the recycled brine was reached, crystallization would initiate in the cyclone and crystals would settle in the conical base area of the quiet zone. Recycled brine was drawn off from the top of this zone and returned to the heater by the centrifugal pump. This process could proceed indefinitely with steady flow rates of distillate, crystalline product and of mother liquor sufficient to maintain about 50 percent of the original salts in the brine (about 111,000 ppm of TDS at the three-fold concentration level). In these tests, however, the needed control instruments for continuous operation were not available, and a batch-wise procedure was adopted.

The crystalline product was removed from the mother liquor by centrifugation. A sample of this product was allowed to effloresce to the anhydride and when analysed showed 97.3 percent Na_2SO_4.

Recrystallization was done by re-dissolving the decahydrate in a small volume of water at about 40°C with continuous stirring. The apparatus used was an open cylindrical vessel (made by silver-soldering a brass plate to one end of a 50-cm long brass pipe of 10-cm diameter), placed in a similar vessel (made from a 15-cm diameter brass pipe) through which hot water was circulated. The decahydrate was recrystallized by recirculating chilled brine through the outer cylindrical vessel and the Plexiglass container in which the cooling coil of the refrigeration unit was submerged as shown in Figure 7. The crystalline $Na_2SO_4 \cdot 10H_2O$ was recovered by centrifuging and allowed to effloresce to the anhydride by exposing it to the air on a sheet of filter paper. This product (oven-dried) analysed to 100.2 percent Na_2SO_4.

In an alternative method of operating this pilot plant, the recrystallization of the decahydrate to produce the anhydride form directly was as follows:

(1) The evaporator was evacuated of air and a concentrated solution of the decahydrate in distilled water was drawn in under vacuum to the level of the cyclone separator.

(2) The feed recirculation pump was started and the immersion heaters were adjusted to heat the feed to about 85°C.

(3) Cold water flow through the condenser coil was then turned on at a flow-rate monitored with a rotameter and adjusted with a valve to ensure that the brine temperature in the cyclone and crystallization vessel stayed about 85°C (185°F) during the rest of the evaporation-crystallization procedure.

(4) The anhydride form of Na_2SO_4 settled in the base of the separation vessel and was recovered through the drain valve and spun free of water in the basket type centrifuge. This finely crystalline material was analyzed and showed 94.45 percent Na_2SO_4.

(b) Adaptation of a Vertical Tube Evaporator Operated by Vapor Compression for Sodium Sulfate Recovery, with Interface Enhancement.

The vapor compression vertical tube foam evaporator VC-VTFE, constructed and tested under a previous EPA-sponsored project in this Laboratory and shown in Figure 8 (4), was modified for this phase of the work. The modifications provided feed brine preheating by counterflow heat exchange with the distillate and blowdown and improved the performance ratio of this equipment by varying the belt drive ratio for a better match between the motor and the compressor (Roots type) available for this evaporator. In earlier use (4), the compressor provided a rather high compression ratio (and ΔT) but for this application it was anticipated that a reduced compression ratio would improve the economy of the VC-VTFE unit. Two sets of V-belt pulleys, adapters, and belts were used in these tests. One set provided a compressor speed of 300 rpm and the other 600 rpm compared with the 915 rpm of the original equipment (4).

The use of the interface-enhanced method of operating an evaporator, also known as vertical tube foam evaporation (VTFE), was described in detail elsewhere (4,5) and has also been the subject of two earlier EPA-sponsored studies in this Laboratory (4,14,16). The substance of the VTFE improvement is to cause the evaporating liquid to flow over a heat transfer surface in the form of a foaming layer of the liquid and its vapor. This mode of two-phase flow is facilitated by the addition of a few parts per million of a selected surfactant or foaming agent. This foamy flow over the heat transfer surface increases the evaporation-side coefficient several-fold and can approximately double the usual overall heat transfer coefficient obtainable without foamy flow in modern evaporators having double-fluted distillation tubes.

In the work discussed here, the VC-VTFE mode of operation was applied to the concentration of softened irrigation drainage water (1,3), and to the evaporatative-crystallization of sodium sulfate anhydride from such a

concentrated brine.

(c) Vapor Compression, VTFE Pilot Plant Used in This Study

In this study, a vertical tube evaporator of 20 cu. m/day (5000 US gallon/day) capacity was operated with a Roots type vapor compressor. The evaporator was rotatably mounted, to permit comparative tests with upflow and downflow modes of feed flow through the distillation tubes. The distillation tubes were double-fluted aluminum-brass, 3.8-cm (1.5-in.) diameter by 1.83 m (6-ft.) heated length (supplied by Yorkshire Imperial Metals, Ltd., Leeds, England). Forty-nine tubes were assembled in a wedge-shaped bundle. These tubes were "O"-ring sealed through naval bronze tube sheets, with the tubes spaced 0.64 cm (0.25-in.) apart on equilateral triangles.

The evaporator, shown in Figure 8, was constructed of type 316 stainless steel and mounted on an A-frame. Rotation of the evaporator unit around the compressed vapor pipe permitted either upflow or downflow operation. For this purpose, two mist eliminators of stainless steel wire mesh were installed at appropriate elevations within the vapor-liquid disengagement vessel. The vapor produced during passage of the liquid through the distillation tubes was separated from the residual liquid in the disengagement vessel and passed upward through the mist eliminator and through a 15.2-cm (6-in.) diameter stainless steel pipe to the compressor. The latter was driven with a 25-hp electric motor at 300, 600 or 900 rpm. A digital, totalizing watt hour meter was provided for the continuous monitoring of compressor energy consumption. The vapor compressor increased the vapor pressure by up to about 34.5 KPa (5 psi); the compression ratio imposed upon the vapor was variable by the experimental use of one or more of three by-pass lines of 5.1-cm (2-in.) diameter with valves which diverted compressed vapor back to the inlet of the compressor.

Different feed distribution devices were preferred for each mode of operation to provide the most effective interface enhancement effects. For the downflow mode used, feed was directed through orifices onto the top tube sheet at locations interstitial of the tubes and then passed into the tubes as annular layers at about 4 liters per tube per minute.

Surfactant additives and their concentration levels were selected to sustain foamy flow within the tubes but not beyond their outflow ends. This limited the foaming agent additive to concentrations below the level where foaming in the vapor-liquid disengagement vessel would present problems such as carry-over and excessive pressure drop. Surfactant concentrations of 15 to 50 ppm were used.

Heat transfer performance data were obtained from temperature measurements and from the rate of condensate flow which was measured directely with a calibrated, in-line cylindrical collection vessel. From this vessel the condensates were either pumped for removal from the system in measured quantities, or for recycle to the feed. Temperature data were obtained with platinum resistance probes having associated bridges and digital voltmeters providing a continuous, direct digital display of the steam-side temperature (Ts) in the tube bundle, the feed temperature (Tf), and the residual brine

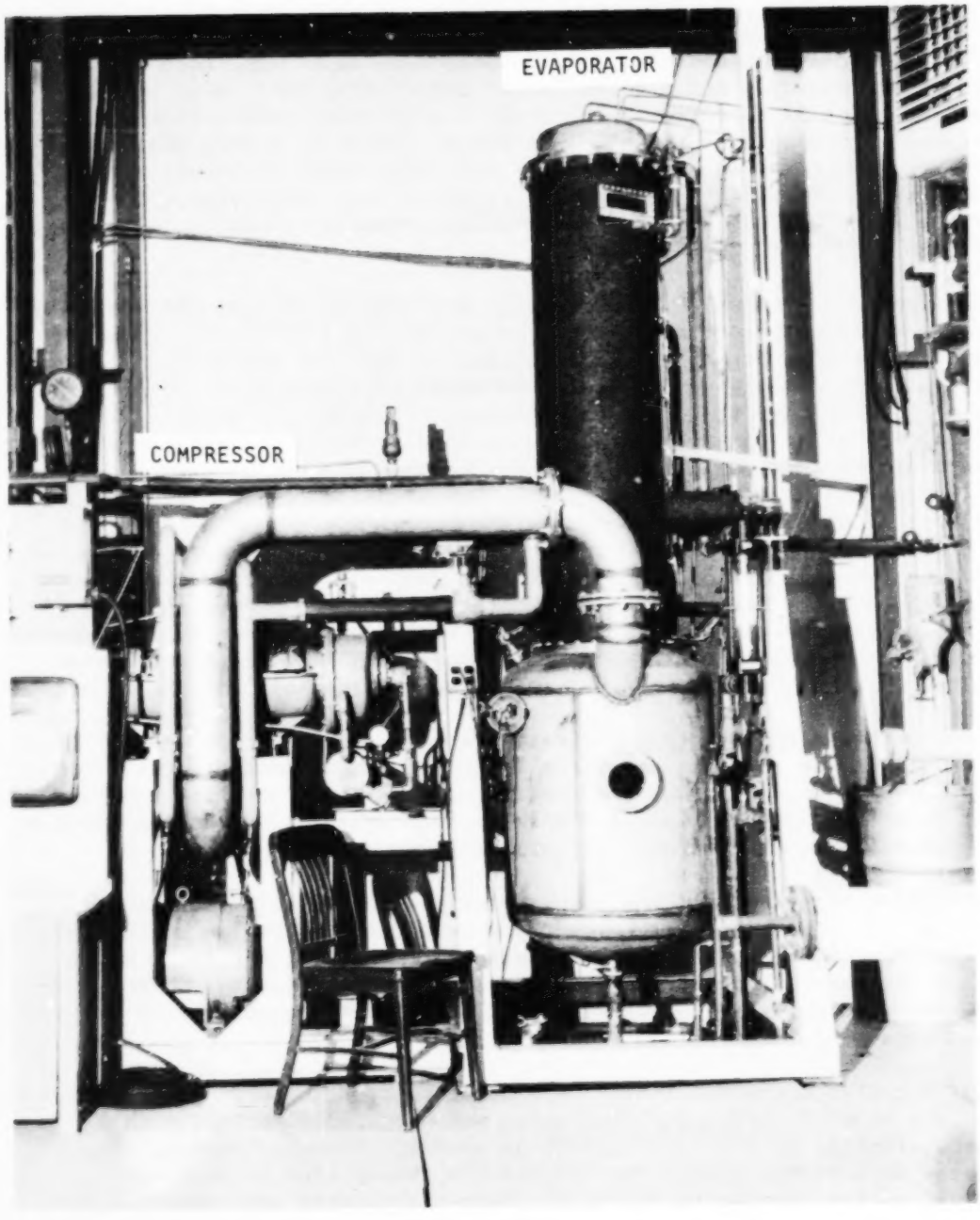


FIGURE 8. VAPOR COMPRESSION VERTICAL TUBE FOAM EVAPORATOR (DOWNFLOW)

temperature (Tb) in the disengagement vessel. These data were checked by means of mercury-filled thermometers also mounted in the individual streams.

The seawater feed was preheated, and the distillate and discharged brine were cooled by counterflow heat exchange, utilizing a plate type heat exchanger having 90-10 copper-nickel plates (supplied by Mechanical Equipment Company (New Orleans, USA) and providing an approach temperature of about 5°C. Further heating and deaeration of thefeed was done by letting it flow downwards as a film over the inside wall of a 7.6 cm (3-in.) diameter copper tube 3.05 M (10-ft.) long, in counter-flow with steam blown upwards through the tube. The degassed, preheated feed was subsequently transferred to the evaporator with a pump at a controlled flow rate. (The evaporator vessel and the vapor compressor were preheated by passing steam into them, followed by draining all condensates before introducing the preheated feed). Additional heating of the feed before start-up was by a steam-heated coil of soft copper tubing mounted into the feed distributor section above the orifice plate. During operation of the VC-VTFE, compressed vapor vented from the tube bundle was passed through this coil before its discharge. The objective of this operation was to maintain the temperature of the recycled residual feed brine close to or slightly above the evaporation temperature in the distillation tubes.

Brine was recycled from the bottom of the disengagement vessel through a 5.1-cm (2-in.) diameter copper tube with a centrifugal pump, and its flow controlled with a valve. This feed was injected into the feed distributor on a tangent, causing swirling flow over the coil heated with vented vapor, and thence through the orifice plate into the tube bundle at a flow of about 3.8-l (1-gal.) per minute per tube.

Several windows mounted on the inlet distributor section and on the disengagement vessel permitted close observation of the vapor-liquid flows.

(d) Crystallization of Sodium Sulfate by Conventional VC-VTE and by the Foamy-Flow Enhanced VC-VTFE Procedure.

The vapor compression vertical tube evaporation (VC-VTFE) facility (see Figure 8) was preheated by passing steam into both the steam- and brine-side and then draining all condensates. The preheated feed, containing 27% sodium sulfate in water, was pumped into the vessel, and circulated through the tubes, its temperature raised to about 103°C by passing steam through the copper tube heating coil located in the brine distributor above the tube bundle. Next, the vapor compressor was turned on and the compressed vapor by-pass valves were closed in sequence, raising the steam-side pressure stepwise to its maximum level. The condensate collected from the steam-side of the tube bundle was returned to the recirculated brine feed until steady-state was established, as indicated by the steam- and brine-side temperatures, the condensate flowrate, and the electrical energy drawn by the VC-motor. Deaeration of the feed by passing of non-condensible gases through the tube bundle to the atmosphere with a small flow of compressed vapor as a bleed-off was usually completed and steady-state established within about 20 minutes. Gradual evaporation-concentration of the brine was then initiated by diverting the distillate (condensate) flow from the brine recycle stream and rejecting it into a

reservoir after measuring its rate of flow. These flow data, temperature data on the steam- and brine-side (Ts and Tb) and the VC energy consumption rate were recorded at about 5-minute intervals during the course of the evaporation-crystallization, as shown in Table 3.

The overall VTE heat transfer coefficient and the VC power consumption were plotted as a function of the feed concentration factor, shown as plots A and B in Figure 9. These results show a continuous increase in the VC energy requirement responsive to the increasing brine concentration due to evaporation. The power consumption per 1000 liters of distillate dips slightly for the brine concentration factors of 1.2 to 1.3 and then rises continuously in inverse proportion to the VTE heat transfer coefficient, U. This is presumably responsive to the brine boiling point elevation due to its increased salinity. Crystallization was initiated at a feed concentration factor of 1.5 and proceeded to a factor of 2.5 at which level the residual brine volume became too small to maintain its recirculation, and the evaporation process was stopped. The accumulated distillates (125 l) were then returned to the brine, reconstituting it to its original 27% concentration level. To this was now added 10 ml of linear alkyl benzene sulfonic acid (99% active) as a foaming agent before repeating the above evaporation-crystallization procedure, this time imposing foamy evaporative two-phase flow of brine downward through the distillation tubes and repeating the data and observations taken above.

The data from the VTFE mode of operation are recorded in Table 4 and plotted as curves C and D in Figure 9. Good foamy flow was observed from the distillation tubes for the first data set (brine concentrations of 1 to 1.1), but little foaminess emitted from the tubes thereafter until crystallization set in (at 1.5). Good foamy flow persisted from here on throughout the crystallization until the process was stopped as before (at 2.5) when the residual brine volume became too small to sustain its recirculation. The data plotted as curve C in Figure 9 shows the overall VC-VTFE heat transfer performance during the gradual evaporation-concentration process; a gradual reduction in performance was again observed responsive to the boiling point elevation requiring gradually increasing ΔT (and Ts). However, this plot shows that whenever foamy flow was maintained, the heat transfer performance was significantly higher than in the previous process (plot A) without surfactant addition and foamy flow. The VC-VTFE performance was typically about 30% higher than the VC-VTE performance during the crystallization stage. These data are consistent with the VC power consumption that was measured directly and independently with a kilowathour meter as plotted in curve D. The latter fell below the energy consumption of the first process series (plot B). During the most significant crystallization stage, VC-VTFE operation showed an energy saving of about 25%.

It was apparent from these data and from other similar experiments with this VC-VTFE pilot plant that foamy flow of the evaporating brine-salt slurry appears to be a prerequisite to enhanced heat transfer performance and VC energy reductions. Such foamy flow was not always readily obtained with brine-solid slurries. It appears that for the most effective use of VTFE for different evaporation-crystallizations, VTFE will need to be pilot plant tested for each application prior to its use. Apparently, the salt

TABLE 3. CRYSTALLIZATION OF Na_2SO_4 BY VC-VTE WITH SLURRY-FEED RECYCLE

Feed: Na_2SO_4, 56.7 kg in tap water, 208 liters (27%)

Time	Ts, °C	Tb, °C	ΔT, °C	Power kWh/h	Distillate l/h	U-Coefficient W/m²-°C	Distillate Liters	Power/Consumption kWh/1000 l	Remarks
10.30	108.4	103.1	5.4	15.86	478.1	5246	11.36	33.18	No Crystallization
10.35	108.8	103.2	5.5	16.39	495.5	5326	22.72	33.08	" "
10.40	109.2	103.4	5.7	16.98	545.0	5627	34.09	31.15	" "
10.45	109.4	103.7	5.8	17.65	592.4	6047	45.44	29.78	" "
10.50	109.6	103.6	5.9	18.20	579.8	5752	56.8	31.39	" "
10.53	109.6	103.5	6.1	19.44	567.7	5485	68.16	34.24	Crystallization
10.57	109.9	103.2	6.7	19.8	567.7	5031	79.52	34.87	"
11.00	109.7	102.7	7.1	20.62	534.5	4474	90.88	38.57	"
11.03	109.6	102.1	7.6	21.6	469.9	3679	102.24	45.97	"
11.06	109.3	101.3	8.0	22.1	446.8	3310	113.6	49.41	"
11.09	109.2	100.7	8.5	23.6	432.6	3021	125.0	54.43	"

TABLE 4. CRYSTALLIZATION OF Na_2SO_4 BY VC-VTFE SLURRY-FEED RECYCLE

Feed: Na_2SO_4, 56.7 kg + Linear Alkyl Benzene Sulfonic Acid, 10 ml in tap water, 208 liters (27%)

Time	Ts, °C	Tb, °C	ΔT, °C	Power kWh/h	Distillate l/h	U-Coefficient W/m²-°C	Distillate Liters	Power/Consumption kWh/1000 l	Remarks
12.08	106.4	102.1	4.3	13.7	594.8	6649	11.36	23.03	No Crystallization
12.17	108.9	102.9	5.9	16.36	592.4	5899	22.71	27.61	" "
12.20	109.2	103.2	5.9	16.74	592.4	5893	34.07	28.27	" "
12.23	109.3	103.4	5.9	17.61	619.4	6217	45.42	28.53	" "
12.26	109.6	103.7	5.8	18.0	592.4	5996	56.78	30.38	" "
12.29	110.0	103.9	6.1	18.62	599.0	5786	68.13	31.10	Crystallization
12.32	109.9	104.0	5.9	19.15	586.1	5871	79.49	32.68	"
12.35	109.6	103.6	5.9	18.95	592.4	5888	90.84	31.97	"
12.38	109.4	103.0	6.4	19.15	573.7	5269	102.20	33.37	"
12.42	109.3	102.4	6.8	19.32	524.1	4524	113.55	36.86	"
12.45	109.1	101.8	7.2	20.62	504.7	4139	125.0	40.87	"

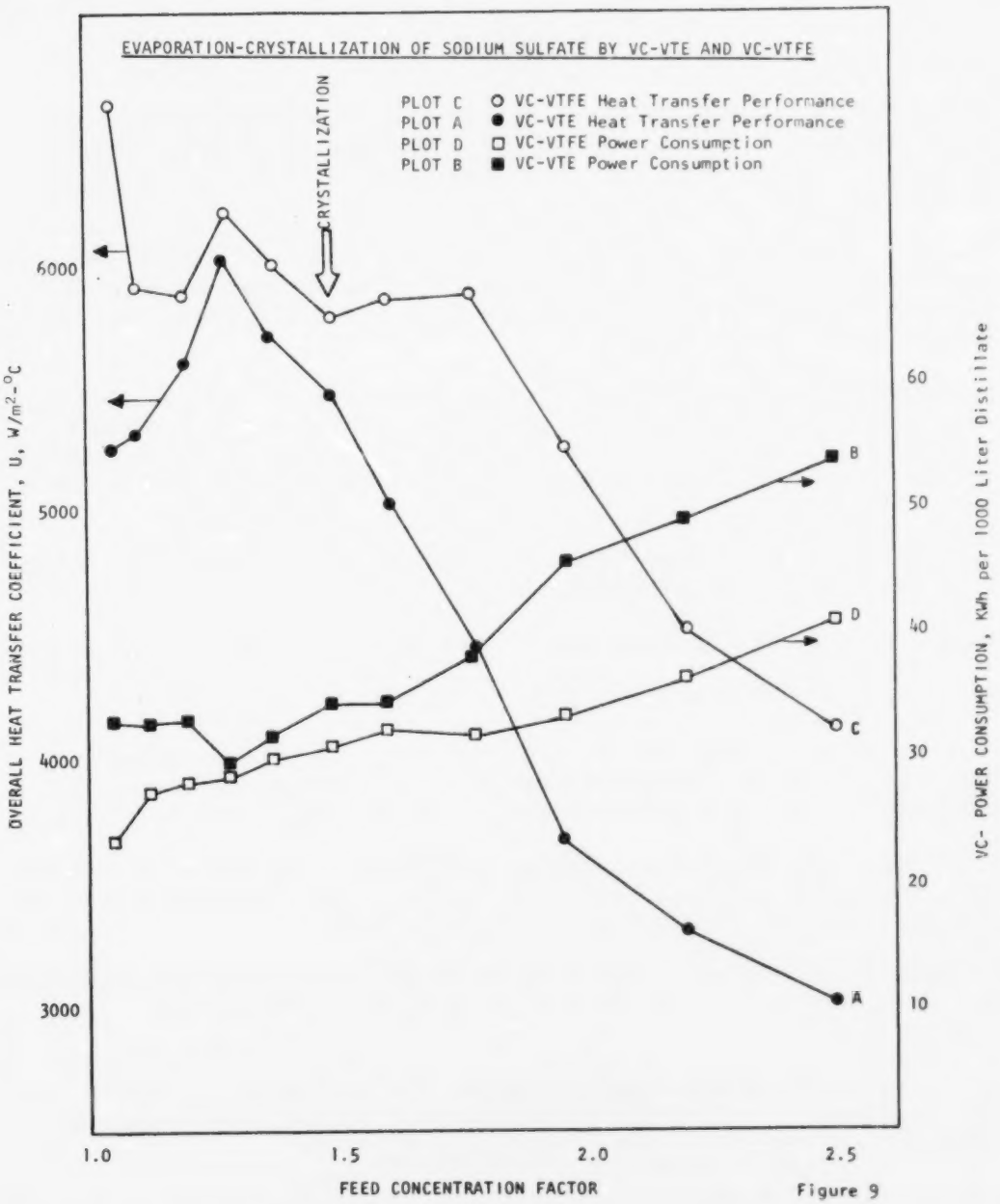


FIGURE 9. EVAPORATION-CRYSTALLIZATION OF SODIUM SULFATE

concentration as well as the surfactant concentration in addition to the ΔT and the heat flux are factors that affect foaminess during VTFE crystallization.

REFERENCES

1. Sephton, H. H., and G. Klein. A Method of Using Irrigation Drainage Water for Power Plant Cooling. In: Proceedings, First Desalination Congress of the American Continent, Mexico City, 1976. Desalination 19:257-268, 1976

2. Klein, G., and H. H. Sephton. Reclamation of High-Sulfate Irrigation Drainage Water for Power Plant Cooling. In: Recent Developments in Separation Science, Calvin Calmon and Harris Gold, Ed. Vol. II, Chapter 6, pp. 61-74, 1979.

3. Lindholm, R., D. Walker, H. H. Sephton and G. Klein. Agricultural Wastewater for Power Plant Cooling: Development and Testing of Treatment Processes. Final Report by the California Department of Water Resources and the University of California Seawater Conversion Laboratory, 106 pp. June 1978.

4. Sephton, H. H. Interface Enhancement Applied to Evaporation of Liquids. U.S. Patent No. 3,846,254, 1974.

5. Sephton, H. H. New Developments in Vertical Tube Evaporation of Seawater. In: Proceedings of the Fifth International Symposium on Fresh Water From The Sea. 2:279-287, Alghero, 1976.

6. Sephton, H. H. Renovation of Power Plant Cooling Tower Blowdown for Recycle by Evaporation-Crystallization with Interface Enhancement. EPA-600/7-77-063, U.S. Environmental Protection Agency. 53 pp., 1977.

7. Notice of Intention of San Diego Gas and Electric Company to File Application of Certification of Sundesert Nuclear Plant, Together With Transmission Lines and Necessary Appurtenances. 1976.

8. Stetson, C. L. Potential Use of Agricultural Waste Water for Power Plant Cooling. California Department of Water Resources Report No. 1972.

9. Stone & Webster Engineering Corporation. Water Treatment Demonstration Facility Report for Sundesert Nuclear Plant. Boston, Massachusetts, 1976.

10. Stone & Webster Engineering Corporation. Conceptual Engineering Cooling System and Associated Water/Waste Treatment Systems for Sundesert Nuclear Plant. Boston, Massachusetts, 1975.

11. Sephton, H. H. The Use of Interface-Enhanced Vertical Tube Evaporation, Foam Fractionation and Ion Exchange to Improve Power Plant Cooling With Agricultural Wastewater. Proposal to the California Department of Water Resources, UCB-Eng-3841, 1975.

12. The California Water Plan - Outlook in 1974. Bulletin Number 160-74. California Department of Water Resources. Summary Report, Table 27, 1974.

13. The California Water Code. Division 1, Chapter 6, Section 461.

14. Valdes-Krieg, E., C. J. King, and H. H. Sephton. Foam and Bubble Fractionation for Removal of Trace Metal Ions from Water. In: Environmental Protection Agency Conference on Traces of Heavy Metals in Water, Removal Processes and Monitoring, Center of Environmental Studies, Princeton University. EPA Publication No. 902/9-74-001, 1973.

15. Sephton, H. H. Recycle of Power Plant Cooling Tower Blowdown with Interface Enhancement. In: Proceedings of the Second National Conference on Complete WateReuse, Chicago, Illinois, 1975.

16. Sephton, H. H. Vertical Tube Evaporation with Fluted Tubes and Interface Enhancement: Comparative Performance of Upflow Versus Downflow of the Feed. ASME Paper No. 75-HT-43, American Society of Mechanical Engineers, New York, N.Y. In: ASME-AIChE Heat Transfer Conference, San Francisco, CA, 1975.

17. Valdes-Krieg, E., C. J. King and H. H. Sephton. Removal of Surfactants and Particulate Matter from Seawater Desalination Blowdown Brines by Foam Fractionation. Desalination, 16:39-53, 1975.

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16. ABSTRACT The report evaluates the feasibility of a novel energy-conserving way to recover useful salts (sodium sulfate and calcium sulfate) from concentrated brines by evaporation/crystallization. The concentrated brines examined were cooling tower blowdown from agricultural wastewater and this blowdown after further concentration and use in ion exchange regeneration. Laboratory and pilot tests were made with both conventional evaporation/crystallization and interface-enhanced, vertical-tube foam evaporation which increases evaporation. Sodium sulfate and calcium sulfate recovery provides potential capital cost savings, about $2 million for a 1000-MWe power plant. Sale of these products is an added incentive to their recovery. The use of foamy vapor/liquid flow on the evaporating brine/crystal slurry enhanced heat transfer by up to 40% and enabled concurrent energy reductions of 28%, compared to conventional evaporation/crystallization of sodium sulfate in a 5000-gpd vapor-compression vertical-tube evaporation pilot plant. Consequently, the use of agricultural wastewater for power plant cooling in the San Joaquin Valley with ion exchange for pre-softening and wastewater regeneration solely with concentrated brine from blowdown appears technically feasible and economically attractive.

17. KEY WORDS AND DOCUMENT ANALYSIS				
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Pollution	Sodium Sulfates	Pollution Control	13B	07B
Waste Water	Calcium Sulfates	Stationary Sources		
Industrial Water	Brines			11G
Agricultural Wastes			02A	
Irrigation	Evaporation		02C	07D
Cooling Water	Crystallization		13A	
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